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Research Article

Catalytic Performance of Calcium-Lanthanum co-doped Ceria ($Ce_{0.85-x}La_{0.15}Ca_xO_{2-\delta}$) in Partial Oxidation of Methane

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Abstract

In this study, $Ce_{0.85-x}La_{0.15}Ca_xO_{2.6}$ was synthesized using sol-gel combustion method and applied for partial oxidation of methane (POM). The physicochemical properties of catalyst were analyzed using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and thermogravimetric analysis (TGA). Material shows a pure cubical structure and is highly stable up to 850 °C. The performance testing indicated the conversion of CH_4 is 65% and selectivity of H_2 and CO are 28% and 8%, respectively. The performance indicated the catalyst has a potential to be used for partial oxidation of methane on a larger scale.

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Keywords: partial oxidation of methane; POM; hydrogen production; Ce0.85-xLa0.15CaxO2-δ

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1. Introduction

The world is starting to accept hydrogen (H_2) gas as the fuel of the future, due to its ability to produce clean energy at higher efficiencies than conventional fuels. However, production of H_2 gas is still a concern that needs to be addressed before the world can look towards it as the primary source of energy.

Even though hydrogen is the most abundant element in the known universe, it rarely exists on its own naturally as H_2 gas, and it must be obtained by reforming or decomposing hydrocarbons [1] and/or water [2]. There are various paths that can be utilized to generate H_2 , but they can be classified into two major classes [3]: (1). Electrolysis – which uses the electric current to break down water molecules into H_2 and O_2 gases; (2). Thermochemical process – which uses heat energy to decompose water or hydrocarbon molecules.

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Methane is a primary source of energy in the world today, however, it is a green house gas (GHG) itself, packing a global warming potential of approximately 28 to 36 over the period of 100 years [4]. This means that 1 ton of CH₄ released in the environment will be responsible for heating up the atmosphere 28 to 36 times more than 1 ton of CO₂ released over the period of 100 years [5]. This is why methane is used to produce H₂, a clean fuel which can more than meet our energy demands. The mostly commonly studied processes for the production of hydrogen are steam reforming, methane decomposition, auto-thermal reforming, methane decomposition by methantropic bacteria and partial oxidation of methane [6-10]. Unfortunately, most of these processes have high energy requirements and produce CO_x and unnecessary coke [11–14].

One of the most accepted methods of H₂ production is from partial oxidation of methane (POM). It is a widely studied technique for the production of H₂ rich syngas [15]. POM is a stable process and requires a lot less energy for the production of syngas as compared to other reforming processes. Furthermore, POM has a very high conversion rate of methane and excellent H₂ selectivity [16]. However, the major concern is carbon deposition and lower H₂/CO ratio which is to be addressed, as reported in literature [17].

Researchers have studied the effect of Cerium and Lanthanum as support for active metal catalysts in the past. However, both of these materials have been studied separately [18–20]. In this study, the Ce_{0.85-x}La_{0.15}Ca_xO₂₋₆ is synthesized with various Ca loading and tested for POM. Calcium doping in the structure has been limited to 10% because higher concentrations of Ca in the structure have been known to form CaO impurity phases [21]. The characterization, such as: XRD, SEM/EDS, and TGA, were performed to analyze its suitability for POM.

2. Materials and Methods

2.1 Synthesis of Ce_{0.85-x}La_{0.15}Ca_xO₂₋₈

In this research, $Ce_{0.85-x}La_{0.15}Ca_xO_{2-\delta}$, where x was taken as 0%, 5%, and 10% for 3 samples, was synthesized using sol-gel aided citric acidnitrate combustion method. Cerium nitrate hexahydrate (Sigma Aldrich), lanthanum nitrate hexahydrate (Sigma Aldrich) and calcium nitrate tetrahydrate (Sigma Aldrich) were all used as metal precursors and citric acid was used as the chelating agent and fuel for the sol-

gel combustion. The samples were abbreviated according to the calcium doping concentrations as per the following codes as mentioned in Table 1.

All metal precursors were mixed in deionized water and continuously stirred for 2 hours at 80 °C. Citric acid was added to the solution in the ratio of 1:1.5 (metal precursors: citric acid) [22] and the temperature was increased to 120 °C. The mixture was further stirred at this temperature for another hour to ensure proper mixing of all precursors with the chelating agent. After this, the temperature was increased to 400 °C and this temperature was maintained until the combustion was completed and yellowish ash was obtained.

After the ash was obtained, the sample was placed in a drying oven at 120 °C overnight to ensure the removal of all moisture from the sample. Based on the TGA results the samples were then calcined in a muffle furnace (Magma Therm, Model: CWF1200, Turkey) at 850 °C for 5 hours to ensure the removal of all volatile compounds present in the sample. The prepared powders were identified as LDC, 5CaLDC, and 10CaLDC.

2.2 Catalyst Characterization

The X-ray diffraction (XRD) analysis was done at room temperature for phase characterization of the prepared LDC, 5CaLDC, and 10CaLDC and catalysts using D8-Advance (Bruker, Germany) having Cu-Kα radiation (λ = 0.15418 nm), while 2θ angle was set from 10° to 80° with a scan rate of 0.2°.s-1. The diffractograms were analyzed using the Jade software (version 6.5). Morphology and elemental analysis of the prepared samples was performed usscanning electron microscope (SEM) (TESCAN VEGA3 LMU) operating at 20kV coupled with energy-dispersive X-ray spectros-(EDX) probe (Oxford Instruments INCAx-act, model 51-ADD0007).

The thermal decomposition behavior of the as calcined LDC, 5CaLDC, and 10CaLDC was investigated via thermogravimetry (Shimadzu, DTG-60H, Japan). The samples (3–5 mg) were heated from 20 °C to 900 °C with a heating

Table 1. Sample Compositions and their codes.

Sample Composition	Sample Code
$Ce_{0.85}La_{0.15}O_{2-\delta}$	LDC
$Ce_{0.80}La_{0.15}Ca_{0.05}O_{2\text{-}\delta}$	5CaLDC
$Ce_{0.75}La_{0.15}Ca_{0.10}O_{2\text{-}\delta}$	10CaLDC

ramp of 10 °C.min⁻¹ in an inert atmosphere using a flow rate of 50 mL.min⁻¹ of nitrogen gas.

2.3 Experimental Setup of Partial Oxidation of Methane

Figure 1 illustrates the schematic diagram of the experimental setup employed for partial oxidation of methane reaction. The reactor is constructed of SS-316 stainless steel tube with a length of 40 cm with an outer diameter of 14 mm and an inner diameter of 12 mm. The reactor was heated using a resistive electrical heating system. The catalyst was loaded into the middle of the reactor tube and was held in position using quartz wool. The reactor temperature was gauged using a thermocouple placed alongside the catalyst bed. The CH_4 and O_2 , both 99.99% pure, were fed into the reactor using a mass flow controller (MF4603-n1-1-bv-a, Servoflo Corporation, USA) to regulate the feed gas flowrate. The product gases were continuously fed into and analyzed using a gas chromatograph (GC-2010 Pro. SHIMADZU Japan) having a Thermal Conductivity Detector (TCD) column (RT-MS5A, 30 m x 0.32 mm ID, 30 μm) which was used to determine the amounts of H₂, CO₂, CH₄, and CO coming out of the reactor column [23]. The conditions at which methane decomposition reaction was carried out are as follows; reaction temperature = 850 °C, catalyst loading = 0.20 g, CH₄ flow rate = 20 mL.min⁻¹.

2.4 Definition and Calculation

To assess the catalytic activity of synthesized samples as partial oxidation of methane

reaction catalyst, methane conversion, hydrogen selectivity, and hydrogen yield were calculated, so that the catalytic performance can be easily visualized. The methane conversion, hydrogen yield, and selectivity were calculated using Eqs. 1-3 [23].

$$CH_4 Conversion(X_{CH_4},\%) = \frac{CH_{4in} - CH_{4out}}{CH_{4in}} \times 100\%$$
 (1)

$$H_2 Yield(Y_{H_2}, \%) = \frac{H_{2out}}{2 \times CH_{Ain}} \times 100\%$$
 (2)

$$H_2 Selectivity(S_{H_2},\%) = \frac{H_2 Produced \%}{2 \times (Converted CH_4)} \times 100\%$$
 (3)

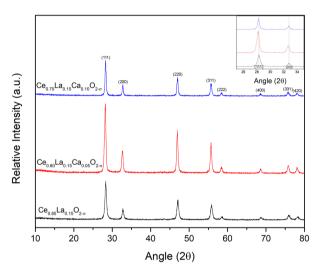


Figure 2. XRD of LDC, 5CaLDC and 10CaLDC.

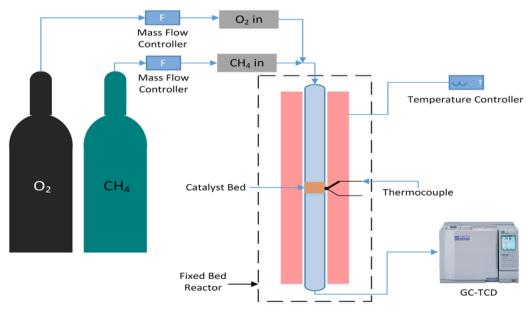


Figure 1. Schematic of experimental setup for Partial Oxidation of Methane.

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3. Results and Discussion

3.1 Material Physicochemical Properties

The structural analysis of all the powders was performed using XRD. Figure 2 shows the XRD patterns of as calcined LDC and calcium doped LDC (5% CaLDC and 10% CaLDC). LDC was identified as $Ce_{0.85}La_{0.15}O_{1.6}$ using JCPDs, comprising of the space group Fm-3m and ref-

erence code 96-900-9009. The peak initially shifts to a lower 20 as Ca is doped onto the structure of the LDC. This can be attributed to the bivalent Ca²⁺ replacing the tetravalent Ce⁴⁺ as can be seen in the inset image of Figure 2 which shows the zoomed in image of the (111) and (200) peaks. The peaks then shift towards a higher angle with an increase in Calcium content due to the larger ionic radii of La³⁺

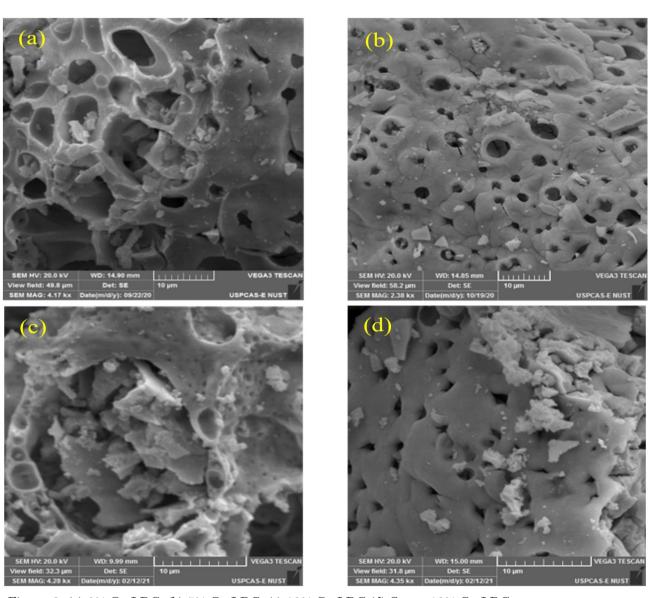


Figure 3. (a) 0% Ca-LDC, (b) 5% Ca-LDC, (c) 10% Ca-LDC (d) Spent 10% Ca-LDC.

Table 2. Lattice parameter and d-spacing for all major peaks for all 3 samples.

	${ m Ce_{0.85}La_{0.15}O_{2}}$		${ m Ce_{0.8}La_{0.15}Ca_{0.05}O_{2}}$		${ m Ce_{0.75}La_{0.15}Ca_{0.1}O_{2}}$	
Peak	Lattice Parameter (Å)	d-spacing (Å)	Lattice Parameter (Å)	d-spacing (Å)	Lattice Parameter (Å)	d-spacing (Å)
111	5.4559	3.14997	5.4815	3.16474	5.46368	3.15446
200	5.45673	2.72836	5.48125	2.74063	5.46477	2.73239
220	5.45756	1.92954	5.47169	1.93453	5.46702	1.93288
311	5.45748	1.64549	5.46888	1.64893	5.46797	1.64866

(1.16 Å) and Ca²+ (1.12 Å) as compared to that of Ce⁴+ (0.970 Å). The lattice constants and the d-spacing of each sample were calculated for all major peaks for all 3 samples and are listed in Table 2. Figure 3 shows the SEM micrographs of the fresh LDC, 5CaLDC, 10CaLDC, and spent 10CaLDC at 10 μm magnifications. The micrographs in Figure 3(a), (b) and (c) depict the fresh LDC catalysts and Figure 3(d) shows the spent 10CaLDC after it underwent the partial oxidation of methane reaction. The synthesized material possesses a highly porous, weblike morphology, ideal for the support required to carry out the partial oxidation of methane reaction [24].

EDX was performed to analyze the elemental composition of 10Ca-LDC before and after it was run in partial oxidation of methane reaction. Figure 4(a) shows the EDX results of the fresh 10Ca-LDC and shows that only Cerium, Lanthanum, Calcium, and oxygen are present. Figure 4(b) shows the EDX of spent 10Ca-LDC the results show that carbon is also detected. Figure 5(a) shows the TGA result for as calcined sample of 10CaLDC. The weight loss is in the range of 5–6% for the powder which can be attributed to moisture loss. The obtained results show that the LDC is highly stable as a

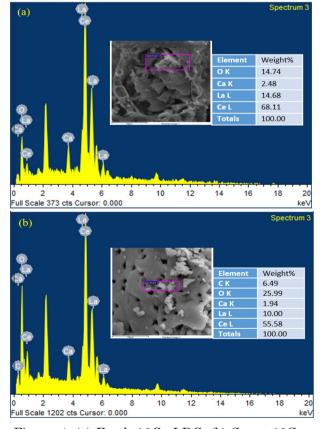


Figure 4. (a) Fresh 10Ca-LDC, (b) Spent 10Ca-LDC.

support at high temperatures as no significant weight loss is observed even at 900 °C. Figure 5(b) shows the TGA curve for the spent 10CaLDC catalyst. As can be seen that approximately 2% weight loss is observed. Almost all of this weight loss can be attributed to carbon. As is evident from the curve the weight loss around 600–700 °C is characteristic of gasification of coke of graphitic carbon.

3.2 Catalytic Activity and Stability

The comparative chart of the catalytic performance showed by LDC, 5% Ca-LDC, and 10% Ca-LDC is shown in Figure 6. The results show that the LDC shows a decent activity for partial oxidation of methane as the conversion is around 65% with H₂ selectivity and CO selectivity 28% and 40%, respectively. However, when the LDC is doped with Ca, the average conversion decreases slightly at around 57% and 62% for 5CaLDC and 10CaLDC, respectively. For 5Ca-LDC H₂ selectivity improves to 32% and for 10Ca-LDC it increases to 34%. The addition of calcium in the LDC structure does decrease the conversion of methane, however,

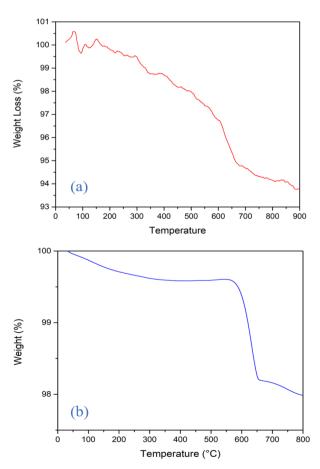


Figure 5. (a) TGA of Fresh 10CaLDC (Calcined) (b) TGA of Spent 10CaLDC.

it improves the selectivity of CO as well as that of H₂. The correlation of the calcium dopant variation with the performance of the catalyst can be verified from the SEM images of the samples in Figure 3. As can be seen that increasing the calcium concentration increases the porosity of the structure, which in turns create more favorable sites that can aid in partial oxidation of methane into syngas. The synergy of cerium and lanthanum supported materials for catalysis have proved to be effective before [25] and hence the material synthesized in this study has the potential for being a very viable support for partial oxidation of methane.

4. Conclusions

The composition with 10% Ca showed best results in terms of $\rm H_2$ selectivity and yield, however it shows partially lower $\rm CH_4$ conversion. As mentioned before, the tests were conducted with no active catalyst loading on the samples and still it showed improved $\rm H_2$ selectivity. Hence, it can be concluded that the LDC, 5Ca-LDC and 10Ca-LDC are all very ideal materials for catalyst support as they show an acceptable stability and decent $\rm CH_4$ conversion even without any active metal catalyst loaded on it.

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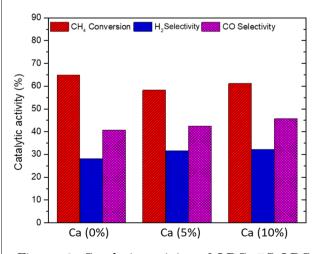


Figure 6. Catalytic activity of LDC, 5CaLDC and 10CaLDC.

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